

# Production of Flame-Retardant Nylon 6 and 6.6

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M. S. SUBBULAKSHMI, NISHKAM KASTURIYA, and HANSRAJ  
Defense Materials and Stores Research and Development Establishment, DMSRDE  
P.O. G. T. Road  
Kanpur 208013, India

P. BAJAJ and ASHWINI K. AGARWAL  
Department of Textile Technology, IIT  
Delhi 110016, India

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## 1. INTRODUCTION

Flame-retardant textiles are important constituents of various protective clothing, particularly for defense applications like clothing for nuclear-biological-chemical warfare, tank crew overalls, tarpaulins, camouflage nets, ballistic and thermal protection wear and also for industrial applications such as thermal protection wear for firefighters, welder's clothing, and for industries having a high risk of fire hazards. These textiles are

also used as tapestry, curtains, and upholstery in hospitals, hotels, and the like. In the United States, even sleepwear needs to be flame retardant.

Every textile fiber type burns differently, and during the burning process, the textile fiber thermally decomposes. This produces different products, including some toxic gases. These toxic gases evolve either from the basic textile substrate or from the flame-retardant chemicals used in the textiles. The casualties during fire are mostly due to inhalation of toxic gases developed during the burning process of the textiles. Many studies have shown that 50–60% of the victims succumbing at a fire die from inhaling smoke and toxic gases and not from direct fire or burns [1]. Therefore, the toxicology of flame-retardant materials must be given more consideration to minimize the hazards, while selecting a suitable flame retardant for any textile. In most of the studies, factors other than flammability have been almost neglected. Therefore, the carcinogenicity and mutagenicity of flame retardants and their possible effects on the environment need to be tested. Toxicity of any burning material is evaluated by measuring the lethality of a material burned under specified combustion conditions, with the test animals inhaling the smoke for a fixed time period. Computer models now exist for rigorous calculation of fire hazards [2].

Generally, polyamides show better resistance to wear and abrasion, low coefficient of friction, good resilience, and high impact strength. Nylon 6 has better thermal and weather resistance in comparison to nylon 6.6; however, nylon 6.6 has higher rigidity than nylon 6. Apart from the above two nylons, other commercially available polyamide fibers include nylon 6.10, nylon 11, nylon 12, nylon 4.6, and aromatic polyamides such as Nomex and Kevlar. Nylon 11 and nylon 12 have been used in the manufacture of electrical insulators, battery casings for aircraft use, and gear wheels for water meters. Nylon 6 and nylon 6.6 represent more than 98% of the total polyamide volume; practically, these two polyamides are used interchangeably in most applications [3, 4]. The aromatic polyamides are essentially used for high-temperature applications like thermal protective clothing, firefighter suits, and some other industrial applications.

Many research papers have appeared in the literature; however, no exhaustive review exists on flame-retardant polyamides. In the present paper, we review the work carried out by various researchers for nylon 6 and nylon 6.6, which are commercially popular fibers.

## 2. THERMAL BEHAVIOR OF NYLON 6 AND 6.6

To select the appropriate flame-retarding agents for nylon 6 and 6.6, it is necessary to understand their thermal behavior. Generally, when the polymeric materials are burned, the gases evolved are CO, NO<sub>2</sub>, HCN, and the like, which are toxic [5]. When different fibers are subjected to the International Organization for Standardization (ISO) "N" gas model test, which is a bench-scale test for toxic potency, it is observed that the evolution of CO differs from fiber to fiber. Among the natural fibers, evolution of CO is greater from cotton than wool. Among the synthetic fibers, the evolution of CO from nylon 6.6 is next only to that from polypropylene. The following important fibers are arranged in decreasing order for the evolution of CO [6]:

Cotton > Polypropylene > Nylon 6.6 > Polyurethane > Polyvinyl Chloride > Wool

Textile fibers can be divided into two classes based on their relative ignitability [7]: (1) fibers that char when ignited, such as viscose, cotton, wool, and the like; and (2)

fibers that melt when ignited, such as polyamides, polyesters, polypropylene, and so on. The chemical composition, bond energies, and intermolecular cohesive forces are some of the factors affecting the flammability of any organic polymer [8–10]. The decomposition of cellulosic material produces levoglucosan and char. As the reaction continues, this levoglucosan further decomposes into large amounts of flammable volatile products that propagate the flame and small amounts of carbonaceous char. In contrast, polyamides, polyester, and the like, being thermoplastic, melt and decompose on ignition. The dripping molten polymer adheres to the skin and greatly aggravates burn injuries of the wearer.

Burning characteristics of various synthetic and natural fibers are given in Table 1. Nylon 6 and nylon 6.6 both soften at 50°C and melt at 215°C and 265°C, respectively. Nylon 6 pyrolyzes above 430°C and undergoes combustion at 450°C. For nylon 6.6, the pyrolysis and combustion temperatures are about 403°C and 530°C, respectively. A pyrolysis temperature is the temperature at which chemical degradation takes place by the action of heat in the absence of air; pyrolysis is the essential first step in the combustion of polymers. The combustion temperature is the temperature at which chemical decomposition takes place by a combination of the substance with oxygen, causing evolution of light and heat during a burning reaction [11, 12]. The limiting oxygen index (LOI) value for the untreated nylon 6 and 6.6 are about 21–22%. The LOI is the minimum percentage of oxygen required in an oxygen-nitrogen mixture to sustain the downward burning of the material. The heat of combustion  $\Delta H$  is 39 kJ/g for nylon 6 and 32 kJ/g for nylon 6.6. The heat of combustion is defined as the energy generated in a flaming combustion process per unit mass of the material vaporized [13].

Among the natural and other conventional synthetic fibers, wool has a maximum combustion temperature of about 600°C and yields higher LOI values (i.e., 25–27%). Acrylics, cotton, and viscose have lower pyrolysis and combustion temperatures, and the LOI value is lower (i.e., around 18–20%). Hence, these fibers catch fire quickly.

### 3. FLAMMABILITY CHARACTERISTICS OF NYLON 6 AND 6.6

Polyamides burn slowly, drip, and may self-extinguish; the difficulty in burning a polyamide is due to the large difference between the melting and ignition points of

TABLE 1  
Thermal Transition Temperatures and Limiting Oxygen Index (LOI) of Some Fibers

Fiber	$T_g$ , °C	$T_m$ , °C	$T_p$ , °C (pyrolysis)	$T_c$ , °C (combustion)	$\Delta H$ , kJg <sup>-1</sup>	LOI, %
Nylon 6	50	215	431	450	39	21–22
Nylon 6.6	50	265	403	530	32	21–22
Polyester	80–90	250–255	400–477	480	24	22
Acrylic	90–100	>320	290	>250	32	19
Cotton	—	—	350	350	19	18–20
Viscose	—	—	350	420	19	18–19
Wool	—	—	245	600	27	25–27

Source: From Refs. 14 and 15.

polyamides coupled with their low melt viscosities [16]. The heat generated during combustion is sufficient to melt the polymer. Nylons also ignite more easily than many natural fibers.

Nylon has self-extinguishing properties due to extensive shrinkage and dripping during combustion [17]. When the nylon polymer is ignited, first it melts, and then the molten droplets drip away from the flame. Quite often, most of the heat is carried away with the droplet, making the material self-extinguishing. However, if the molten droplets burn continuously, this will promote a greater fire hazard.

Although the nylon fiber has self-extinguishing properties, there are serious problems when it is blended with nonthermoplastic fibers owing to the "scaffolding effect" [18–20, 45]. For example, cellulose fibers char, and this carbonaceous char acts as a supporting structure that causes the molten polymer to remain exposed to the flame, and thus the blend burns vigorously.

Nylon 6 has a lower melting point than nylon 6.6, and this may be one of the reasons for the difficulties in rendering flame retardancy to nylon 6 compared to nylon 6.6 [21].

Under vacuum at temperatures above 300°C, the main decomposition products released by polyamides are about 95% nonvolatiles [22–28]. The volatile products mainly consist of CO<sub>2</sub>, CO, water, ethanol, benzene, cyclopentanone, ammonia, numerous other aliphatic and aromatic hydrocarbons, and saturated and unsaturated molecules [29, 30].

However, when polyamides are heated at temperatures below 200°C in the presence of oxygen, the degradation patterns are different [31, 32]. Thermal oxidation shows the volatile products to be as follows: water 52%, CO<sub>2</sub> 33%, CO 12%, and methanol, formaldehyde, and acetaldehyde are around 1% each. Photooxidation and irradiation of low molecular weight polyamide suggest that the most labile hydrogen atom in the polyamide molecule is on the carbon atom adjacent to the —NH group [33–35]. When nylon is pyrolyzed the process causes depolymerization [36].

The suggested oxidative decomposition mechanism for nylon is given in Fig. 1 [37].

Levantovskoeya assumed that, in analogy with the oxidative degradation of hydrocarbons, the oxygen molecule initiates the chain process of oxidation of polyamides (Eq. 1 in Fig. 1). At the point of abstraction of the hydrogen atom, either a peroxide radical or a hydroperoxide is formed (Eqs. 2 and 3, Fig. 1). During the decomposition of hydroperoxide, water is formed (Eq. 4, Fig. 1). The formation of water can lead to the hydrolysis of the polymer that, on decarboxylation, produces CO<sub>2</sub>. In addition to the decomposition of peroxide, breakdown of peroxide radicals may also take place. The peroxide radical may isomerize by the reaction with the free valence of the adjacent C—C bond. Isomerization and breakdown of the peroxide radical result in chain rupture, which in turn forms a molecule with a terminal aldehyde group (a) and a radical (b) (Eq. 5 in Fig. 1). The decomposition of (a) leads to formation of CO (Eq. 6, Fig. 1). Radical (b) can break down with the rupture of the C—C bond and the formation of a second C—O bond, which leads to the production of formaldehyde (Eq. 7, Fig. 1).

#### 4. FLAME-RETARDANT NYLON 6 AND 6.6

##### 4.1. Flame-Retardant Mechanism

Natural fibers and conventional man-made fibers (e.g., polyester, polyamide, acrylic, polypropylene, and rayon) are liable to ignite in different ways, so different

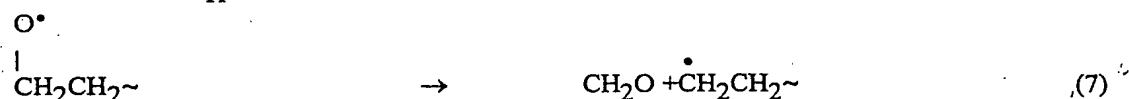
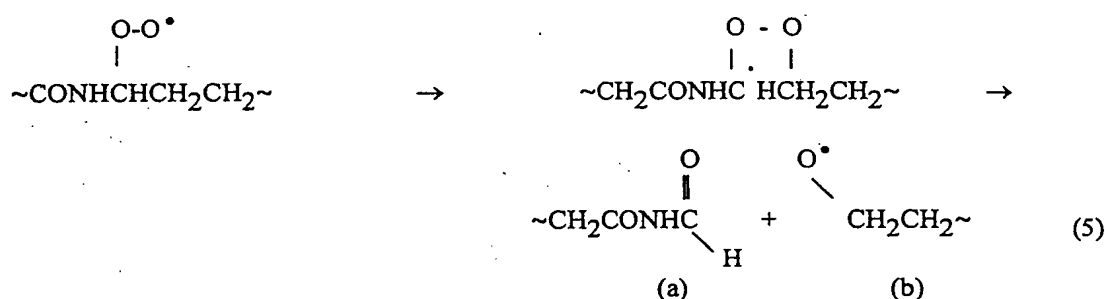
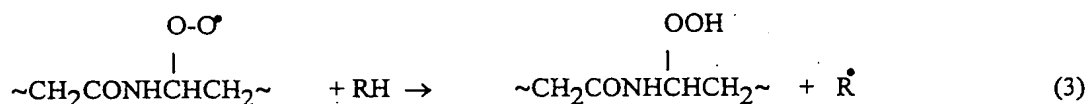
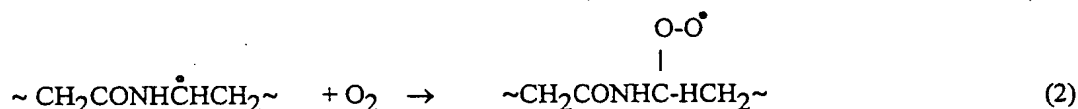
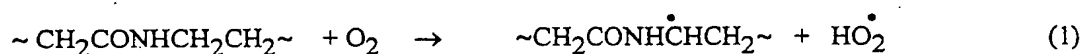


FIG. 1. Suggested oxidative decomposition mechanism for nylons.

flame-retardant mechanisms are found operative in different fibers. Study about the mechanism of action of various flame retardants on textiles is therefore essential to evaluate a particular flame-retardant system. The two mechanisms of flame retardancy are (1) gas/vapor phase mechanism and (2) solid/condensed phase mechanism.

The flame retardant acting in the gas phase mechanism generally does not change the thermal decomposition of a polymer, and the volatile gas output remains virtually the same. In the gas phase mechanism, during the combustion process, the textile material consisting of a flame-retarding agent decomposes into free radicals due to heat. These free radicals combine with atmospheric oxygen/air through complex reactions. Thus, the oxygen then combined is unavailable for the oxidation of flammable gases generated by the decomposition of polymer substrate and hence retards the combustion process [38].

The condensed phase mechanism involves changes in the polymer substrate. Systems that promote extensive polymer cross-linking at the surface form a carbonaceous char on heating. Char insulates the underlying polymer from the heat of the flame, preventing production of new fuel and further burning. Other systems evolve water during

heating, cooling the surface, and increasing the amount of energy needed to maintain the flame [39].

Flame-retardant fibers can be generally classified into two classes [40]: (1) inherently flame retardant fibers, like aramides, PBI (polybenzimidazole), polyamide-imide, and the like; and (2) fibers with chemical structure or surface characteristics that have been chemically modified to make them so.

The first group possesses some entirely new properties; they are called high-performance fibers [41]. The second group retains most of the properties of the unmodified fiber, which could be nylon, polyester, acrylic, viscose, or others. Aramids are used for flame-retardant protective clothing due to their high-temperature resistance and high tenacity. They are also used in composite materials, such as personal armor and vehicle armor against ballistic attack, due to their high strength-to-weight ratio [42]. The flammability profiles of aramid fibers and nylon are depicted in Fig. 2 [43].

#### 4.2. Production of Flame-Retardant Nylon Fibers

Flame-retardant behavior can be rendered to the second group of fibers (i.e., conventional polyester, polyamide, acrylic, etc.) in three different ways [44, 45]: (1) at the polymerization stage using certain phosphorus- and/or halogen-based comonomers in the fiber-forming polymers; (2) by adding flame-retardant additives in the spinning dope/spinning bath before extrusion; (3) surface treatment or topical finishing using flame-retardant finishes. Table 2 gives the various possible ways of rendering fire resistance to conventional synthetic fibers according to the method and the nature of the polymeric substrate [17].

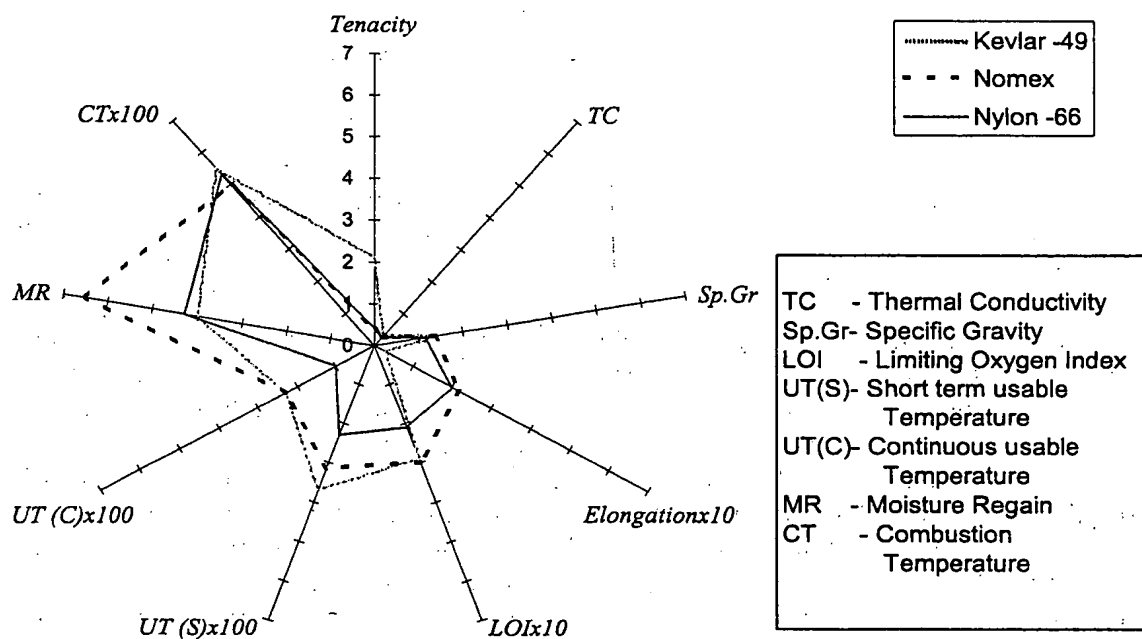


FIG. 2. Flammability profiles.

#### 4.2.1. Modification During Polymerization

Synthetic fibers may be made effectively flame retardant by polymer modification, so that the polymer easily drips away from the flame during its exposure to heat. For this purpose, halogenated compounds have been found very effective [46–48]. These compounds operate through the vapor phase mechanism. On heating, the halogenated compounds decompose and give rise to free radicals. These free radicals react with oxygen and prevent the inflammable volatile gases developed during burning of the material from oxidation. Thus, the combustion of burning substrate is retarded. The halogenated compounds exhibit synergistic flame-retardant effects when used with antimony oxide.

The flame-retarding agents used for nylon during the polymerization process are red phosphorus and phosphorus-containing compounds like bis(2-carboxyethyl) methyl phosphine oxide (CEMPO). The major problems when halogenated compounds are used arises from the dehalogenation and dehydrohalogenation reactions that can occur at high temperatures, and they are not stable enough to be held under vacuum at a high temperature for a long time during spinning [49].

It is assumed that the red phosphorus exhibits a vapor phase mechanism of flame retardancy in oxygen-containing polymeric substrates like polyester, polyamides, polyurethane, and the like [50], whereas the condensed phase action of red phosphorus has been proposed for nonoxygenated polymers like polyacrylonitrile [51–53]. Red phosphorus is highly explosive, and its use for flame retardancy as such is dangerous. So, it is mixed with an inert synergist like magnesium hydroxide or aluminum trihydrate. A number of flame-retardant chemicals are used for nylon 6 and nylon 6.6 during the polymerization process (Table 3).

$\epsilon$ -Caprolactam undergoes anionic polymerization in the presence of 5 wt% red phosphorus and 5 wt% magnesium oxide to give flame-retardant nylon 6 with an LOI of 28.5% [49]. The process is initiated by sodium or lithium caprolactamate and activated by *N*-acetyl caprolactam (both 1 mol% on the basis of monomer). The particle size of red phosphorus is less than 40  $\mu$ .

Marik et al. [54] prepared fire-retardant polyamides by the anionic polymerization of 9.5:0.5 caprolactam-lauro lactam melt, homogenized with 0.5 mol% toluene diisocyanate (TDI), caprolactam–red phosphorus mixture with 1.5% phosphorus content in the polymer and 0.25 mol% catalyst sodium dicaprolactamo-bis(2-methoxy ethoxy) aluminate and heating at 240°C.

TABLE 2  
Methods of Adding Fire Resistance

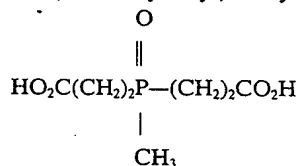
Flame retardant method	Polyamide	Polyester	Acrylic
Copolymerization	(+)	++	++
Spinning dope/bath	(+)	+	+
Topical finishing	+	+	(+)

++, important; +, less important; (+), minor importance.

TABLE 3

Modification During Polymerization

Reagents	Properties	Reference
$\epsilon$ -Caprolactam + 5 wt% Red Phosphorus + 5 wt% MgO $\xrightarrow[\text{Polymerization}]{\text{Anionic}}$ Flame-retardant Nylon 6	LOI 28.5%	49
9.5:0.5 Caprolactam-lauro lactam + 0.5 mol% TDI + Caprolactam Melt-Red Phosphorus (1.5%) Mixture + 0.25 mol% Sodium Dicaprolactamo-bis-(2-Methoxy Ethoxy) Aluminate	FR properties achieved	54
Nylon 66 salt + 30 mol% CEMPO <sup>a</sup> + HMD + Water	LOI 25.3%  Tenacity 2.8 gpd Boiling water shrinkage 40% Moisture regain 7% (at 65% RH) Melting point 225°C	55

<sup>a</sup>Bis(2-carboxy ethyl)methyl phosphine oxide (CEMPO), mp = 175°C–177°C:

Nylon 6.6 is made flame retardant by melt polymerizing nylon 6.6 salt with 30 mol% CEMPO and hexamethylene diamine (HMD). Water is added to make a total charge of 75% of polymer [55]. The finished polymer is extruded and drawn to approximately 4.5 times over a hot pin at 60°C–90°C, which gives a fiber of LOI 25.3% and melting temperature of 225°C. Fiber properties are not much affected up to 35 mol% of CEMPO.

#### 4.2.2. Modification During Spinning

It is an economical method to incorporate flame-retarding agent in the molten nylon while spinning/extrusion to yield a durable treatment. Most of the phosphorus, metal, and halogen additives, however, are not stable at the fiber-spinning temperature. Moreover, their presence changes the properties of the polymer considerably. Hence, one has to carefully select low molecular weight phosphorus, halogen, and inorganic com-



pounds to balance the benefits of the flame-retarding nylon with the adverse side effects caused by these additives to the polymer property.

Some of the flame-retardant additives used in the spinning dope are low molecular weight phosphorus compounds, chlorinated polyethylene, brominated pentaerythritol, antimony oxide, and so on (Table 4).

Butylkina, Ivanova, and Tyuganova [56] investigated the flammability characteristics of the nylon 6 fiber in the presence of various phosphorus-containing flame-retardant additives such as (i) lead methyl phosphonate, (ii) a complex compound of an alkyl phosphonic acid and antimony, (iii) phosphorylated pentaerythritol (fostertrol), and (iv) the phosphorus-containing compound borofos.

Compounds (i) and (ii) belong to the class of nonmelting compounds and (iii) and (iv) are highly viscous liquids. They suggested that it is advisable to use 25% by weight of borofos or 25% by weight of the complex salt of an alkyl phosphonic acid with antimony since these two compounds markedly reduce the rate of decomposition by causing intensive char formation by the polymer. All four flame-retardant additives are stable at the fiber-spinning temperature. The most marked change in  $T_g$  from 52°C–68°C

TABLE 4  
Modification During Spinning

Reagents	Properties	Reference
(i) Polycapraamide + 25% by wt Borofos (Phosphorus-Containing Compound)	Increase in $T_g$ 52°C–68°C	56
(ii) Polycapraamide + 25% by wt of Complex Compound of an Alkyl Phosphonic Acid and Antimony	LOI 29–30%	
75 parts Nylon 6 + 15.25 parts Chlorinated Polyethylene (25% Cl) + 7.75 parts Kemgard 425 <sup>a</sup> + 2 parts Additives (master batch), 1:11.5 master batch:Nylon 6 melt spun	FR properties achieved	57
Nylon 6 + 20% Chlorinated Polyethylene (25% Cl) + 10% Basic Calcium Zinc Molybdate + 2.7% Additives	Class I in ASTM-E-648 testing method	58
Polycapraamide Melt + Mixture of 25 wt% of 4 mol Boric Acid, 1 mol Brominated Pentaerythritol, 0.1 mol Antimony Oxide	LOI 29% Pyrolysis time 30 min Reduction in maximum rate decomposition 17 to 9 mg/min Apparent activation energy of the thermooxidative decomposition process $E_a$ 74.5 kJ/mol (initial material 97.3 kJ/mol)	59
Nylon 6 + 0.6% of 97.7% Red Phosphorus at 230°C	FR properties achieved with self-extinguishing time of 5 s	60

<sup>a</sup>Calcium zinc molybdate ( $\text{CaO} \cdot \text{ZnO} \cdot m\text{MoO}_3 \cdot n\text{H}_2\text{O}$ ); white powder; insoluble in water; density 3 g/cm<sup>3</sup>.

was observed on introduction of borofos, but it does not change the molecular packing coefficient of the nylon 6, which varies from 0.64 (original) to 0.67 (for fiber-containing borofos). The complex salt of an alkyl phosphonic acid and antimony has greater flame-retarding efficiency than fostertrol. The LOI in the case of samples using any of these compounds is 29–30%, while the “phosphorus” present in the complex salt of an alkyl phosphonic acid and antimony is half of the phosphorus present in fostertrol. It is due to antimony-phosphorus synergism taking place in a complex salt of an alkyl phosphonic acid and antimony.

Wells and Cole [57] disclosed in their patent a method for producing flame-retardant nylon 6 fiber that retains good breaking strength. This fiber was prepared by first producing a master batch from 75 parts nylon 6, 15.25 parts chlorinated polyethylene (25% Cl), 7.75 parts KemGard 425 (calcium zinc molybdate), and 2 parts other additives. A mixture of 1:11.5 master batch and nylon 6 was then melt spun. The percentages of zinc, molybdenum, and chlorine in the nylon 6 fiber were 0.01–2.9%, 0.002–0.58%, and 0.05–1.3%, respectively. They also produced flame-retardant nylon 6 by varying the additive levels to 20% chlorinated polyethylene (25% Cl), 10% basic zinc molybdate, and 2.7% other additives, and the product was class I by the ASTM-E-648 testing method [58].

A ternary combustion fire-retardant system consisting of boron, antimony, and bromine was developed by Tyuganova et al. [59]. A 25 wt% mixture of 4 moles boric acid, 1 mole brominated pentaerythritol, and 0.1 mole antimony oxide was introduced into the nylon 6 melt and was spun at a temperature of 235°C on a laboratory melt-spinning rig. There was not much change in the physicommechanical properties. The maximum LOI of the fiber was 29%. A binary system consisting of boric acid and brominated pentaerythritol exhibited an LOI of 25%, but when boric acid has been replaced by antimony oxide, the system exhibited an LOI of 26% (in the modified fiber, the boron content was 2.28%, bromine 3.09%, and antimony 2.61%). It has been suggested that ternary flame retarders of antimony halides or oxyhalides exhibit effective free-radical inhibition on the thermooxidative decomposition of the modified polymer. The advantage of the selected flame-retarder system is the absence of acid hydrolysis of the amide bond in the polycapromide and a decrease in the degree of polymerization (DP) during the fiber spinning. The amounts of toxic gases like CO and HCN were also considerably reduced.

Marik and coworkers [60] extruded nylon 6 (water extractable 1.2%, moisture 0.2%, melting temperature 217°C, and DP 150) with 0.6% of 97.7% red phosphorus at 230°C. The fiber showed a self-extinguishing time of 5 s.

#### 4.2.3. Surface Treatment/Topical Finishing

Generally, there is a problem of polymer degradation with the spinning dopes containing flame retardant. Hence, topical finishing or posttreatment commonly are proposed for conferring flame retardancy to nylon fabrics. The treatment of the nylon fabrics with thiourea-based (Fig. 3a) condensation products with formaldehyde or urea, melamine (Fig. 3b), and their methylolated derivatives has generated interest [61]. A number of finishing agents used for nylon fabric are given in Table 5.

Hydroxy methylation of nylon 6 was performed with formaldehyde (36%) at 70°C–80°C and at a pH of 0.9–1 for 1–2 h. This was followed by treatment with pyrovatex CP (*N*-methylol dimethyl phosphonopropionamide) (10–50%) for 5–30 min and drying at 150°C–180°C for 2–6 min. The product has an LOI of 31.4%, while nylon 6 treated only with formaldehyde gave an LOI value of 23.6% [62].

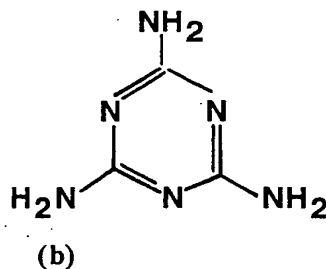
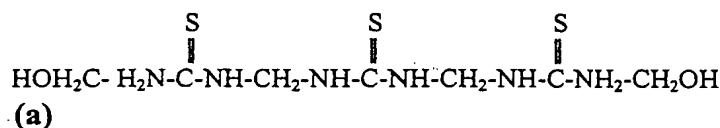


FIG. 3. (a) Methylol thiourea; (b) melamine (2,4,6-triamino-1,3,5-triazine).

Efros et al. [63] treated the nylon 6 fiber with the solution of boric acid polyester (BAP) (Fig. 4) containing boron, chlorine, and nitrogen. The best flame-proofed properties of nylon 6 fibers were attained at a chlorine/boron ratio of 3:20 and a nitrogen/boron ratio of 1:4 in the BAP. The treated fiber has an LOI of 28.2%. The maximum decomposition rate of BAP-treated nylon 6 fiber is reduced from 16 to 6.5 mg/min. In BAP-treated fiber, the yield of caprolactam during the pyrolysis process is reduced almost three times, and this ensures the increase in fire resistance.

Flame-retardant nylon fabric was also produced by treatment with an aqueous solution containing 18.3% Tetrakis Hydroxymethyl Phosphonium Chloride (THPC), 8.5% trimethylol melamine (TMM), 8.8% urea, and 0.1% of a surfactant [64–68]. It was applied on to the fabric by a pad-dry-cure method in which drying was done at 110°C and curing at 145°C. At this temperature, THPC polymerizes with TMM with the evolution of hydrochloric acid. Urea is employed to tie up this hydrochloric acid.

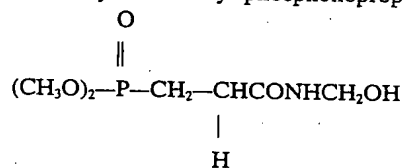
Cross-linkable organophosphorus compounds based on 1,3,5-triacryloylhexa hydro-1,3,5-triazine and dialkyl phosphine oxide have also been used as flame-retardant finishes for polyamides [69]. Novolak or epoxy resins containing 1.7% red phosphorus have also been reported as a flame-retardant finish for nylons [70].

El-Garf and El-Kemry [71] modified the nylon 6 fiber by treating with 2,5-dichlorobenzenesulfonyl chloride (DBSC), which had a great effect on heat and chemical stability of the fibers. They obtained the best results with a DBSC concentration of 25%, a reaction temperature of 115°C, and a treatment time of 4 h. It was found that increasing the DBSC concentration and temperature was more effective because of the increase in sulfur content in modified fibers than increasing the reaction time. Thus, the modified fiber contained 4.9% sulfur and 26.4% carbon residue (a measure of flame retardancy) and had a 97.5% degree of crimp. It also lost solubility in formic acid, concentrated mineral acids, and aqua regia. The fibers only glowed and charred without losing fiber form when put in direct flames, and there was no melting up to 1000°C. The activation energy of decomposition  $\Delta E$  was 194 kJ/mol compared to 46 kJ/mol for the unmodi-

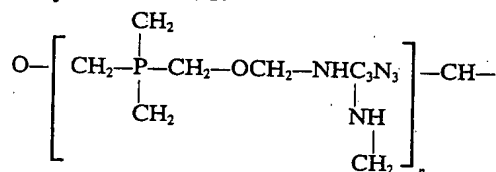
TABLE 5  
Surface Treatment/Topical Finishing

Finishes	Properties	Reference
Treatment with HCHO (36%) + 10.50% Pyrovatex CP <sup>a</sup>	LOI 31.4%	62
Treatment with boric acid polyesters (BAP)	LOI 28.2% Relative breaking load 36.8 CN/tex vs. 44.4 CN/tex of untreated Decomposition rate of fiber reduced from 16 to 6.5 mg/min	63
Treatment with 18.5% THPC <sup>b</sup> + 8.5% trimethylol melamine (TMM) + 8.8% urea + 0.1% of surfactant	FR properties achieved	64-68
Treatment with cross-linkable organophosphorus compounds based on 1,3,5-triacryloylhexahydro-1,3,5-triazine and dialkyl phosphine oxide	FR properties achieved	69
Treatment with Novolak or epoxy resins containing 1-7% red phosphorus	FR properties achieved	70
Treatment with 25% 2,5-dichlorobenzenesulfonyl chloride at 115°C for 4 h	Activation energy of decomposition $\Delta E$ 194 kJ/mol No melting up to 1000°C Glowed and charred without losing fiber form, 10% loss in tenacity	71
Phosphorylation of polyamide	Decomposition temperature 350°C Melting temperature 258°C-270°C	75

<sup>a</sup>N-Methylol-dimethyl phosphonopropionamide [92]:



<sup>b</sup>Polymerized THPC:



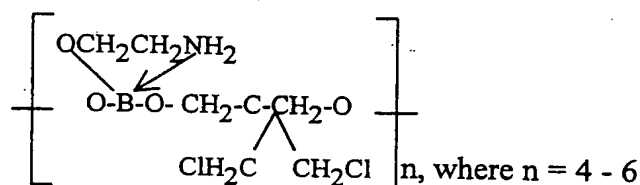


FIG. 4. Boric acid polyester.

fied fibers. However, there was about 10% loss in strength properties, specifically tenacity, which could be due to chemical degradation. The fire resistance of the treated fiber is due to the introduction of an aromatic ring containing sulfur into the polyamide polymer chain, cross-linking of the fibers, or cyclization of the polyamide [72-74]. Belgium [75] revealed that, when polyamide is phosphorylated, its melting temperature increases from 258°C to 270°C, and the decomposition temperature increases to 350°C.

#### 4.3. Manufacture of Flame-Retardant Nylon Plastics

Nylon plastics are commonly used in the composite field as reinforcement thermoplastics and also are used as cables in the electrical and electronic industries. Flammability of nylon plays a crucial role in these fields, too. Hence, it is worthwhile to know the additives used to impart flame retardancy on the thermoplastic nylons.

The flammability tests in the textile industry are completely different from those used for reinforced plastics. A better method of evaluation for materials used in the electrical industry involves the use of Underwriters Laboratories Subject 94 Test [76].

The test method is described [77, 78] as placing a sample (127 × 13 × 3 mm) vertical to a small Bunsen burner flame for 10 s; the sample is ignited at the bottom and burns. If the specimen self-extinguishes within 30 s, another 10-s application is made. Flaming droplets are allowed to fall on a dry absorbent surgical cotton located 300 mm below the sample. The rating is then made as follows:

UL-94, V-0: The average burning time is less than 5 s, and the drips do not ignite the cotton.

UL-94, V-1: The time is less than 25 s, and the drips do not ignite the cotton.

UL-94, V-2: The sample is extinguished, but the cotton is ignited.

The various additives used in flame-retardant nylon plastics are given in Table 6. The high amounts of additive adversely affect the crystallinity of nylon polymers, which is an essential parameter for fiber formation. In nylon 6, the amide linkage is quite reactive, and this is the site where often the flame-retardant additive interaction occurs [79]. This prevents the use of many flame-retardant polyamides for spinning into fibers, and they can be only used for preparing moldings. There is a wide range of flame-retardant additives for polyamide plastics, most of which are used before extrusion of the polymer melt.

Hochberg and Mason [80] prepared a flame-retardant nylon composition by blending 81.45 parts nylon 6 (80% amine terminated) with 14 parts poly(pentabromo benzyl acrylate), 3.5 parts antimony oxide, 0.05 parts calcium chloride, 0.25 parts potassium iodide, and 0.75 parts zinc stearate, and then the mixture was extruded. The prepared

flame-retardant nylon composition showed a UL-94 flammability rating V-0, while nylon with 50% terminal amine groups gave a rating of V-2.

Nylon 6 was blended at 125 parts to 13.6 parts  $\text{Ph}_2\text{Si}(\text{OH})_2$  (and/or a low molecular weight phenyl-substituted siloxane diol), 6.8 parts magnesium stearate, 27.4 parts aluminum trihydrate (ATH), and 20.6 parts deca bromodiphenyl oxide (DBDPO), conditioned in boiling water for 2 h, and placed under ambient conditions for 2 days; it had a UL-94 rating of V-0 and a self-extinguishing time of 4.8 s [81].

Nylon 6 mixed with 20% ammonium polyphosphate (APP) and talc showed a UL-94 rating of V-0 [82]. A chemical reaction of APP with talc was detected in the mixture above 350°C, which prevents the volatilization of polyphosphoric acid.

The effect of the fire-retardant APP on the thermal decomposition of aliphatic nylon 6 was studied by Levchik et al. [83]. They described that the intumescent behavior induced by APP in mixtures with nylon 6 is responsible for its fire-retardant action. From the thermal analysis results, it was observed that an intumescent char was formed on the surface of the burning specimen even in the presence of as little as 10% APP. Further, it showed that the presence of APP destabilizes nylon 6 and modifies its thermal degradation behavior by lowering the activation energy. From this study, they concluded that APP is an ineffective fire retardant at concentrations below 30% in nylon 6, but increasing the concentration to 40% increases the LOI from 23% to 40% and induces intumescent behavior in the burning material. APP favors the formation of caprolactam as the major volatile product against chain fragments, but it does not seem to increase the yield of residue, which is thermally stable at 550°C. The composition of volatile combustible products obtained from nylon 6 is modified by the presence of APP; however, the amount of volatile product is not affected.

In a patent, Pohl [84] disclosed the method of producing a flame-retardant polyamide composition with good mechanical properties by mixing nylon 6 with the lubricant calcium stearate, the fire-proofing agent melamine cyanurate, and glass fibers in an extruder. A reinforced flame-retardant polyamide composition was also prepared by Williams Ian [85] with nylon 6.6-nylon 6 copolymer (90:10) 53%, glass fibers 20%, melamine sulfate 20%, chlorocyclopentadiene-cyclo-octadiene condensation adduct (dechlorane plus) 4%, and zinc borate 3%. The total composition was mixed and extruded at 250°C–270°C. The UL-94 rating for the specimen was V-0. Another patent [86] described flame-retardant polyamide prepared from adipic acid-caprolactam HMD polymer by the addition of 25 parts melamine cyanurate, 3 parts dechlorane plus, 1 part antimony oxide, and 20 parts glass fiber. The resultant polyamide shows a rating of V-0 in the UL-94 test and an LOI of 27%.

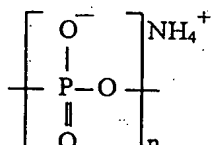
Horacek and Reichenberger [87] added a mixture of two additive dicyanadiamide and melamine to the polyamides (e.g., nylon 6, nylon 6.6, nylon 12) to increase the fire resistance without affecting the mechanical properties or appearance. Ceric et al. [88] produced flame-resistant polyamide by adding antimony oxide and stannous chloride to poly-ε-caprolactam melt.

Grundman et al. [89] produced a flame-retardant polyamide composition by blending 84 parts nylon 6 with 12 parts of 3,4,5,6-tetrabromo-*N*-(2,4-diamino-1,3,5-triazine-6-YL) phthalimide and 4 parts of antimony pentoxide. The flame-retardant polyamide produced showed V-0 rating in the UL-94 test, but when antimony pentoxide was not added to the composition, the resultant flame-retardant polyamide exhibited a V-2 rating in the UL-94 test. Another flame-retardant [21] nylon 6 was prepared with 79% nylon 6, 15% dechlorane, 4% Flamtard S (Alcan Chemicals Ltd., Chalfont Park, Bucks, Eng-

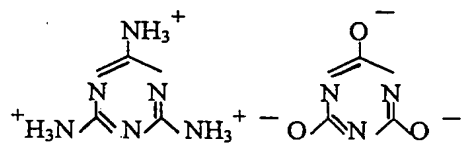
TABLE 6  
Manufacturing of Flame Retardant Nylon Plastics

Reagents	Properties	Reference
81.45 parts Nylon 6 (80% Amine Terminated) + 14 parts Poly(Penta Bromo Benzyl Acrylate) + 3.5 parts $\text{Sb}_2\text{O}_3$ + 0.05 parts $\text{CaCl}_2$ + 0.25 parts KI + 0.75 parts Zinc Stearate <sup>a</sup>	UL 94 rating V-0 vs. V-2 using nylon with 50% amine terminated	80
125 parts Nylon 6 + 13.6 parts $\text{Ph}_2\text{Si}(\text{OH})_2$ (and/or a low molecular weight Phenyl-Substituted Siloxane Diol) + Magnesium Stearate <sup>b</sup> 6.8 parts + 27.4 parts ATH <sup>c</sup> + 20.6 parts DBDPO <sup>d</sup>	UL 94 rating V-0 Self-extinguishing time 4.8 s	81
Nylon 6 + 20% APP + Talc	UL 94 rating V-0	82
40% APP <sup>e</sup> + Polyamide 6	LOI 40% Thermally stable up to 550°C	83
Nylon 6 + calcium stearate + Melamine Cyanurate <sup>f</sup> + Glass fiber	Good mechanical properties	84
53% Nylon 6.6-Nylon 6 (90:10) + Glass fibers 20% + Melamine Sulfate 20% + Dechlorane Plus <sup>g</sup> 4% + Zinc Borate ( $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ ) 3%	UL 94 rating V-0	85
Adipic Acid-Caprolactum-HMD Copolymer + 20 parts Glass fibers + Melamine Cyanurate 25 parts + 3 parts Dechlorane Plus + 1 part $\text{Sb}_2\text{O}_3$	UL 94 rating V-0 LOI 27% Tensile strength 123 MN/m <sup>2</sup>	86
Nylon 6/Nylon 6.6/Nylon 12 + Dicyandiamide <sup>h</sup> + Melamine <sup>i</sup>	No change in mechanical properties and appearance	87
Poly $\xi$ -caprolactum + $\text{SnCl}_2$ + $\text{Sb}_2\text{O}_3$	FR properties achieved	88
84 parts Nylon 6 + 12 parts 3,4,5,6-Tetrabromo- <i>N</i> -(2,4-Diamino-1,3,5-Triazine-6-YL) Phthalimide + 4 parts $\text{Sb}_2\text{O}_3$	UL 94 rating V-0	89
79% Nylon 6 + 15% Dechlorane + 4% Flamtard S <sup>j</sup> + 2% Zinc Borate	UL 94 rating V-0	21
Nylon 6 + 15-20% Poly ( <i>p</i> -Phenylene sulfide) (PPS)	Enhanced tensile and flexural properties	90
Nylon 6 + Magnesium Sulfate + $\text{Sb}_2\text{O}_3$ + Zinc Oxide/ Zinc Borate/Ferric Oxide/Iron Oxide/Zinc Stannate/ Zinc Molybdate	FR properties achieved	91

<sup>a</sup> $(\text{CH}_3(\text{CH}_2)_{16}\text{COO})_2\text{Zn}$ , mp 125°C; <sup>b</sup> $(\text{CH}_3(\text{CH}_2)_{16}\text{COO})_2\text{Mg}$ , mp 145°C; <sup>c</sup>Decomposes above 230°C [93]; <sup>d</sup>Br content 83%, mp 295°C-305°C, decomposition point ca. 425°C [94].

<sup>e</sup>  white powder, starts decomposing at 250°C,  $n > 100$ , commercially known as PHOS-CHECK4, P 32%, N 15.7%, H 4% [96, 97].

<sup>f</sup> Melamine cyanurate:



<sup>h</sup>Hooker Chemical Corp., mp 480°C [98]; <sup>i</sup>mp 208°C-211°C,  $(\text{H}_2\text{N})_2\text{C}=\text{NCN}$ ; <sup>j</sup>mp 347°C; <sup>k</sup>Alcan Chemicals Ltd., Chalfont Park, Gerrards Cross, Bucks, England.

land), and 2% zinc borate. In this case, flame-retardant rating was V-0 on the UL-94 test.

Srinivasan, Vasantha Kumari, and Uthaih [90] incorporated 15–20% poly(*p*-phenylene sulfide) (PPS) in nylon 6, which provided flame-retardancy and enhanced the tensile and flexural properties. PPS is characterized by its good heat, flame, and chemical resistance, as well as electrical insulation properties. It has been observed that magnesium sulfate, antimony oxide, and zinc oxide/zinc borate/ferric oxide/iron oxide/zinc stannate/zinc molybdate also provide flame retardancy to nylon 6 [91].

## 5. SUMMARY

Flame retardancy in nylon fiber and plastics was studied. The effect of various flame-retardant chemicals during the polymerization, spinning, and finishing stages has been thoroughly investigated to select suitable processes and chemicals for flame retardancy of nylon 6 or nylon 6.6 fibers. Generally, phosphorus-based compounds are added during the polymerization stage to achieve flame-retardant nylon fibers. Red phosphorus and magnesium oxide addition during the polymerization stage of nylon 6 polymer gives a fiber with good flame retardancy and an LOI of 28.5%. The flame-retardant additive for addition at the spinning dope stage has to be stable at the melt spinning temperature, so the choice of chemicals becomes limited. The use of a complex compound of an alkyl phosphonic acid and antimony at the spinning dope stage gives flame-retardant nylon fiber having an LOI of 29–30%. The addition of chlorinated polyethylene and zinc molybdate in the spinning dope was also found effective. An interesting effect is seen when a boric acid, brominated pentaerythritol, and antimony trioxide combination was added in a spinning dope of nylon 6; the resultant flame-retardant fiber had an LOI of 29%, but if any of the compound was not added, the LOI was reduced to 25–26%. The high thermal stability required for the flame-retardant additives may be dispensed with using surface finishing, which is supposed to be a more convenient and easier method. In this method, the choice of chemicals becomes wide. The treatment with thiourea-based condensation products is very popular for flame retardancy of nylon fabric. The other effective method is hydroxymethylation of nylon fabric with formaldehyde, followed by treatment with pyrovatex CP. It gives an excellent flame retardancy to nylon and an LOI of 31.4%.

Nylon plastics may be rendered flame retardant by the addition of poly(pentabromo benzyl acrylate), antimony oxide, small amounts of calcium and potassium halides, and zinc stearate in the polymer mixture before extrusion. Addition of aluminum trihydrate and DBDPO was also effective for the purpose. Nylon 6–nylon 6.6 copolymer may be made flame retardant by addition of glass fiber, melamine sulfate, chlorocyclopentadiene-cyclo-octadiene, and zinc borate.

Recent awareness regarding the environment has led to a search for eco-friendly flame-retardant chemicals. Some eco-friendly chemicals like APP and poly(vinyl alcohol) have emerged as low-hazard flame retardants for nylon plastics, but the use of these flame retardants for fibers could become infeasible due to their adverse effect on rheological properties of the polymer and, in turn, fibrillization. Therefore, the search for an eco-friendly flame retardant for nylon fibers needs more effort.



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GARTH L. WILKES

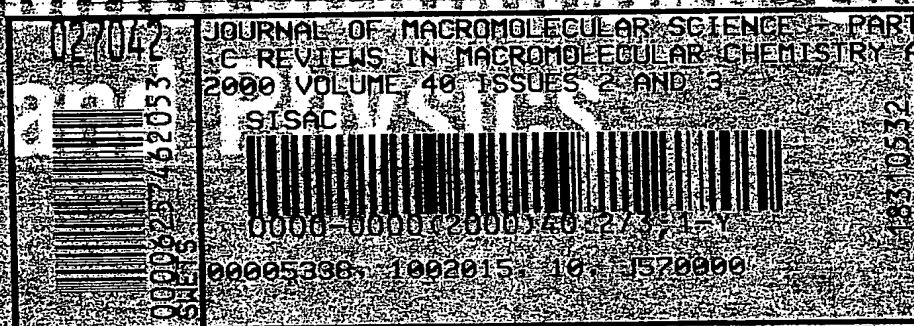
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